Short-Lived Oxygen Diffusion During Hot, Deep-Seated Meteoric Alteration of Anorthosite

Claudia I. Mora,[1]* Lee R. Riciputi,[2] David R. Cole[2]

Heterogeneous oxygen isotope compositions of plagioclase from the Boehls Butte anorthosite include some of the most oxygen-18–depleted values (to −16 per mil) reported for plagioclase in meta-igneous rocks and indicate high-temperature ($T > 500°C$) isotopic exchange between plagioclase and nearly pristine meteoric fluid. Retrograde reaction-enhanced permeability assisted influx of meteoric-hydrothermal fluids into the deep-seated anorthosite. Isotopic gradients of about 14 per mil over 600 micrometers in single crystals require short-lived (about 10^4 years) diffusional exchange of oxygen and locally large effective water:rock ratios, followed by rapid loss of water and cessation of oxygen diffusion in the anorthosite.

Infiltration of surface-derived fluids into hot rocks can cool the rocks as well as cause extensive mineralogical and chemical changes. These effects are controlled predominantly by the temperature of the infiltrating fluids, the permeability of the rocks that are infiltrated, and the extent of fluid-rock interaction and are most significant at shallow levels of the crust (*1*). Penetration of surface-derived fluids into deep, hot (>10 km depth; $T >$ 500°C) rocks is not well understood. It may accompany early retrograde cooling and uplift (*2–4*) and cause isotopic depletion of rocks along detachment faults in metamorphic core complexes (*5–7*). We report results of an ion-microprobe study of oxygen isotope ratios in metamorphosed anorthosite that demonstrate deep, but transient, penetration of surface-derived fluids, which triggered plagioclase recrystallization and a brief period of water-enhanced diffusion.

The Boehls Butte anorthosite is exposed in a fault-bound block uplifted into metasediments along the northern border of the Idaho batholith. This anorthosite experienced a complex, polymetamorphic history, reaching peak *P-T* conditions (event M2) of 650° to 750°C, 8 to 11 kbar (0.8 to 1.1 GPa) (*8*) as a result of the cumulative effects of regional magmatism and crustal shortening. Regional extension accompanying tectonic denudation and emplacement of the latest stages of the batholith at relatively shallow levels in the crust led to a protracted, nearly isothermal decompression under fluid-absent conditions [event M3; $T = 650°$ to 750°C, 4 to 6 kbar (*8, 9*)], followed by a final, rapid stage of decompression, fluid infiltration, and cooling (*9*).

The most distinctive feature of the anorthosite is the coexistence of two different plagioclase phases (Fig. 1): andesine (An_{34-48}) and anorthite (An_{92-98}) (*10*). Andesine occurs as megacrysts, 2 to 25 mm in diameter, with fine-grained (0.1 to 0.2 mm in diameter) granoblastic-polygonal anorthite crystals forming thin (<3 mm thick) patches and layers between megacrysts and also occurring as inclusions in the megacrysts. The presence of anorthite constrains the bulk of the interaction between anorthosite and aqueous fluids to temperatures in excess of 500°C (*11*). There are only trace amounts of secondary minerals, such as chlorite, calcite, and epidote, that are diagnostic of lower temperature ($T < 500°C$) alteration by hydrothermal fluids (*1*); however, rapid and high-temperature decompression may continue to favor the stability of plagioclase.

Unaltered igneous anorthosite from locations throughout the world typically has uniform $\delta^{18}O$ values in the range of +5.8 to +7.6 per mil (*12*). In contrast, oxygen isotopic heterogeneity occurs at several scales within the Boehls Butte anorthosite. Whole-rock plagioclase analyses (*13*) of samples collected over a 12 km^2 area vary from −7.0 to +6.2 per mil, with differences of up to 11.9 per mil in samples located 250 m apart. No clear pattern of alteration relative to geologic contacts or faults can be established. At the scale of a hand sample (~1000 cm^3), bulk separates of andesine and anorthite (*13*) have isotopic fractionations of −0.9 to +2.2 per mil, suggesting wholesale alteration of anorthosite at this scale. However, secondary ionization mass spectrometry (SIMS) measurements indicate intergranular variability of 3 to 15 per mil between plagioclases of like composition (andesine or anorthite) on the scale of a thin section (2.5 cm diameter). The variability of isotopic compositions observed at all scales suggests that the anorthosite interacted with a complexly channelized, meteoric-hydrothermal fluid system (*14*).

Within a single thin section of massive anorthosite, two steep isotopic gradients (15 per mil/600 μm and 13 per mil/400 μm) have been identified along traverses between the interiors of andesine crystals and their contacts with fine anorthite crystals (Fig. 2). The low $\delta^{18}O$ values in this sample, with one spot as low as −16 per mil, are some of the most ^{18}O-depleted values reported for plagioclase in meta-igneous rocks (*15*). Tertiary meteoric water near the Idaho batholith is estimated to have had a $\delta^{18}O$ value of ~−16 per mil (*16*). Thus, these low values indicate that the sample exchanged with nearly pristine meteoric water at temperatures in excess of ~500°C (*15*).

The scale and timing of isotopic exchange with meteoric-hydrothermal fluids are constrained by rates of oxygen isotope diffusion in plagioclase and the conditions under which the measured isotopic heterogeneity might be preserved. Microscale isotopic gradients in andesine were modeled as diffusion profiles (Fig. 2) developed at 550°C between andesine having $\delta^{18}O$ close to the original, igneous value and an extremely ^{18}O-depleted aqueous fluid (*17*). Low $\delta^{18}O$ values for the rims of andesine megacrysts require high water-rock ratios, at least in the local environment of the grains analyzed. Under these conditions, the time required to generate the diffusion profiles is short, generally 10^3 to 10^4 years (Fig. 2). High water:rock ratios cannot persist, however, because wet diffusion at high temperature would rapidly homogenize isotopic gradients in the plagioclases we measured, which have grain radii of 0.5 to 1 mm (Fig. 3).

Oxygen diffusivity may be significant

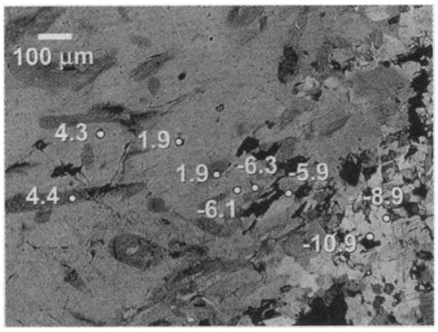

Fig. 1. Photomicrograph showing an andesine megacryst and many fine anorthite grains, and oxygen isotope compositions measured by SIMS. Bar, 100 μm. Anorthite layers are interpreted to be the foci of high-temperature, retrograde fluid-rock interaction, on the basis of isotopic compositions and gradients, cathodoluminescence, and inferred mineral reactions.

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[1] Department of Geological Sciences, University of Tennessee, Knoxville, TN 37996–1410, USA. [2] Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831–6365, USA.

*To whom correspondence should be addressed. E-mail: cmora@utk.edu

even at low fugacities of water (f_{H_2O} = 10 to 500 bar) (*18, 19*); the presence of up to 10% hydrous phases, such as hornblende and biotite, in the anorthosite indicates that f_{H_2O} was not zero. For partial pressures of water as low as 1 bar, the oxygen isotope profiles still indicate short-lived diffusion of $\sim 10^5$ years (Fig. 2). Only if water fugacities are low enough to decrease diffusion rates by several orders of magnitude (dry diffusion; Figs. 2 and 3) can these sub-millimeter–scale isotopic heterogeneities be preserved in plagioclase. The preservation of extreme isotopic gradients at high temperatures of interaction suggest inflow of meteoric fluids, then rapid loss of water and cessation of isotopic exchange; in effect, a nearly instantaneous change from a wet to a dry system, with the consequence of much slower diffusion rates and smaller domains of isotopic equilibration in the dry system (Fig. 3).

Penetration of surface-derived fluids into deep-seated rocks is most commonly associated with detachment faults in metamorphic core complexes (*5–7*) or other large, crustal shear zones (*2, 4*). Fluid dynamic calculations (*3*) indicate that infiltration is also possible in the early retrograde environment. As the mechanical behavior of rocks becomes brittle, the rocks fracture and fluid pressures change from lithostatic to hydrostatic, creating conditions more favorable to transport of fluids into higher temperature environments. Anorthite layers in the Boehls Butte anorthosite are inferred to have been the foci of retrograde fluid flow, on the basis of isotopic compositions and cathodoluminescence textures and spectra (*20*). Reaction of Na-plagioclase with CaCl-bearing hydrothermal brines very rapidly forms anorthite + quartz, a reaction having a negative volume change of reaction (*21*). We suggest that this retrograde, reaction-enhanced permeability may have enhanced the transport and focusing of retrograde fluids.

Thus, microscale oxygen isotope gradients indicate that (i) meteoric-hydrothermal alteration occurred after the peak of metamorphism, under conditions appropriate for post-M3 rapid uplift [$T \approx 550°C$, $P_{total} = 2$ to 4 kbar, $P_{fluid} < 1$ kbar (*8, 9*)] of the terrane; (ii) transport of pristine meteoric water into the anorthosite occurred at temperatures and pressures close to the brittle-ductile transition; (iii) modest to large effective water:rock ratios were responsible for isotopic resetting, particularly in local environments where extreme isotopic depletion is observed in andesine megacrysts juxtaposed with anorthite layers; and (iv) rapid and essentially complete loss of water led to the effective cessation of oxygen isotope exchange after hydrothermal exchange (*22*).

Rapid cooling rates suggested for the Boehls Butte area, about 75°C/Ma (*23*), are best accounted for by the presence of a fluid and advective cooling during rapid uplift of the terrane. This raises an apparent contradiction: the inferred cooling rates require infiltration and advective cooling over a period of at least 2 million years before the system begins to close to O and Ar diffusion, but the preservation of the steep oxygen isotopic gradients we report require a rapid change to fluid-absent conditions at high temperatures early in this period of cooling. The results suggest that retrograde fluid flow is spatially variable, following different pathways at different times in the uplift, resulting in a complex interplay between retrograde fluid flow, cooling, and isotopic exchange.

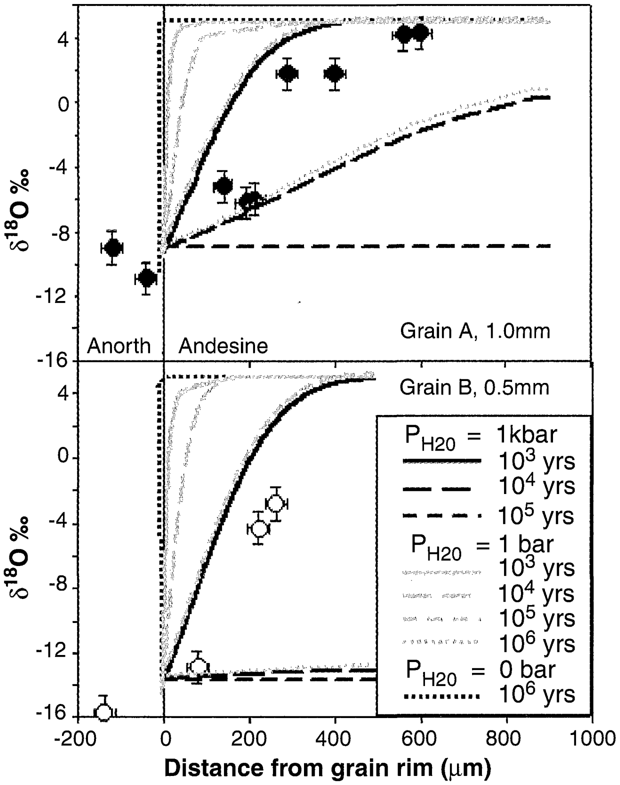

Fig. 2. Plot of oxygen isotope compositions versus distance to andesine-anorthite grain boundary (boundary at 0 μm) for andesine grains of radius 1.0 mm (top) and 0.5 mm (bottom). T = 550°C; P_T = 3 kbar. Error bars are ±1 per mil and ±15 μm. The data are compared to gradients modeled for diffusion in andesine under wet conditions (P_{H_2O} = 1 kbar), conditions of low water fugacity (P_{H_2O} = 1 bar), and dry conditions (P_{H_2O} = 0).

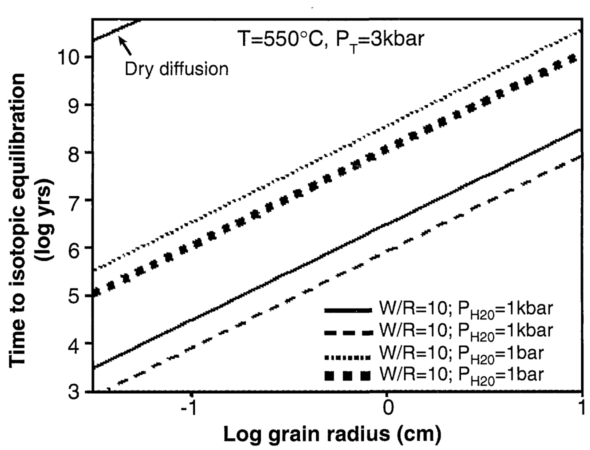

Fig. 3. Plot of plagioclase (andesine) grain radius versus the time to isotope equilibrium, or homogenization of isotopic compositions across the grain. These curves indicate that oxygen isotopic compositions in plagioclase will homogenize on the scale of 1 mm in less than 1 million years, even for nearly dry conditions (P_{H_2O} = 1 bar). W/R indicates water:rock ratio (by weight).

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24. Supported by NSF grant EAR-8922638 and an Oak Ridge Associated Universities Faculty Participation Program Fellowship to C.I.M., NSF grant EAR-9706077 to L.R.R., and the Office of Science, Basic Energy Sciences, U.S. Department of Energy under contract DE-ACO5-96OR22464 with Oak Ridge National Laboratory, which is managed by Lockheed Martin Energy Research Corporation.

16 July 1999; accepted 21 October 1999

Surfactant-Mediated Two-Dimensional Crystallization of Colloidal Crystals

Laurence Ramos,[1]* T. C. Lubensky,[1] Nily Dan,[2] Philip Nelson,[1] D. A. Weitz[1]†‡

Colloidal particles can form unexpected two-dimensional ordered colloidal crystals when they interact with surfactants of the opposite charge. Coulomb interactions lead to self-limited adsorption of the particles on the surface of vesicles formed by the surfactants. The adsorbed particles form ordered but fluid rafts on the vesicle surfaces, and these ultimately form robust two-dimensional crystals. This use of attractive Coulomb interaction between colloidal particles and surfactant structures offers a potential new route to self-assembly of ordered colloidal structures.

The self-assembly of colloidal particles is a promising route to materials synthesis that combines considerable flexibility in the choice of materials with the opportunity to create highly ordered structures on length scales from nanometers to micrometers. Self-assembled structures can form resilient coatings, templates for growth of ordered micro- and nanoporous materials (*1*), and even photonic devices (*2–4*). Self-assembly depends critically on thermal energy; the resultant motion allows particles to attain the optimum positions to create desired highly ordered structures.

To exploit thermal motion, great care must be taken in controlling the interaction energies between the particles themselves and between the particles and their surroundings. Thermally induced self-assembly typically requires repulsive or only very weakly attractive interactions. Strong attraction usually leads to the formation of highly disordered aggregates, rather than ordered colloidal crystal structures. Because of this, attractive Coulomb interactions, which are strong on thermal scales, are usually not effective in producing self-assembled, ordered structures. Thus, for example, when charge-stabilized colloidal particles are mixed with surfactants of the opposite charge, they typically destabilize and form disordered fractal aggregates (*5*) because the surfactant binds Coulombically to the particles. This process makes their surfaces hydrophobic and leads to strongly attractive interparticle interactions.

Because of this expectation of destabilization, few studies of mixtures of particles and oppositely charged surfactants have been reported. However, surfactants can self-assemble into a rich array of structures, and the possibility of the interaction of these structures with the oppositely charged colloidal particles is ignored in the disordered-aggregate scenario. Indeed, recent studies of mixtures of positively charged lipids with negatively charged DNA have shown that highly ordered structures can ensue (*6*, *7*).

We report the unexpected formation of large colloidal crystals when aqueous charge-stabilized polystyrene latex particles are combined with a mixture of an oppositely charged and a neutral surfactant, which self-assemble into vesicles. Surprisingly, exclusively two-dimensional (2D) colloidal crystals are formed. Coulomb attractions cause the adsorption of particles onto the vesicle surfaces, which mediate the formation of 2D crystals. We propose a model that accounts for the observations made during several steps in the sequence resulting in the 2D crystals. This new route to self assembly may serve as a template for the synthesis of novel ordered structures.

We used a mixture of two surfactants: didodecyldimethylammonium bromide (DDAB), a cationic, double-chained amphiphile, and polyoxyethylene (9-10) *p-tert*-octyl phenol (Triton X-100, or TX), a nonionic, single-chained amphiphile. These surfactants have similar areas per polar head group (0.6 nm^2) and similar critical micelle concentrations (cmc) (*8*). Above the cmc, DDAB alone self-

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[1] Department of Physics and Astronomy, University of Pennsylvania, 209 South 33rd Street, Philadelphia, PA 19104, USA. [2] Department of Chemical Engineering, Drexel University, Philadelphia, PA 19104, USA.

*Present address: Groupe de Dynamique des Phases Condensées, (CNRS-UMII) cc26, Université Montpellier II, place E. Bataillon, 34095 Montpellier Cedex 5, France.

†Present address: Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

‡To whom correspondence should be addressed. E-mail: weitz@deas.harvard.edu

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